

PATENT SPECIFICATION

(11) 1416709

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- (21) Application No. 48531/72 (22) Filed 20 Oct. 1972
- (31) Convention Application No. 2152914 (32) Filed 23 Oct. 1971 in
- (33) Germany (DT)
- (44) Complete Specification published 3 Dec. 1975
- (51) INT CL² C23F 11/00 B05D 7/14 B32B 15/04 C08K 5/42
- (52) Index at acceptance



C7E 11
 B2E 193 197 19Y 209 20Y 327 339 380 382 386 38X 38Y
 39Y 410 412 416 41X 41Y 42X 442 44Y 456 463
 46Y 498 507 50Y 518 53X 579
 C3R 38B2B 38C 38D3A 3C C11 C12 C13M C13S C14B
 C25 C28X C29 C6X C9X L2X L6G

(54) CORROSION INHIBITORS

(71) We, BASF FARBEN & FASERN AG, a German Company, of Hamburg, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

5 The invention relates to corrosion inhibitors for the production of coatings for protecting metals, especially iron, and particularly to a process for the protection of metal surfaces.

10 Many inorganic and organic compounds are known as corrosion inhibitors. Amongst the inorganic compounds, examples which are particularly popular are red lead, strontium chromate, lead silicochromate, zinc potassium chromate, zinc phosphate and lead phosphite. Amongst the organic compounds which have been used for protection from corrosion there are the relatively expensive nitro compounds such as, for example, the barium salt of nitrophthalic acid or metal salts, including also the iron salt of nitrophenols, such as alpha-nitro-beta-naphthol.

15 Despite the large number of known substances which are active as corrosion inhibitors, there is a need to develop even more active inhibitors, since industry constantly makes higher demands on the corrosion resistance of such inhibitors.

20 In very recent times, the demand for physiologically harmless and non-toxic agents, in particular, has increased since many of the known protection agents have an injurious effect on health and their use is, for this reason, not entirely safe in many cases.

25 The present invention is therefore concerned with providing a corrosion inhibitor which shows an improved corrosion-inhibiting action as compared to the known inhibitors and produces coatings for protecting metals, especially iron, which meet the raised standards. The corrosion inhibitor in addition should be physiologically harmless and be capable of being produced simply and cheaply.

30 According to the invention there is provided a corrosion inhibitor composition comprising, as the corrosion-inhibiting compound, a water-insoluble complex compound of 1 - nitroso - 2 - naphthol or of an alkaline earth metal salt of 1 - nitroso - 2 - naphthol - 6 - sulphonic acid with a metal cation, wherein the metal is iron, aluminium or zinc, particularly iron, in admixture with a liquid carrier incorporating a film forming substance as hereinafter described.

35 Apart from the complex compounds containing iron as the metal cation, those which contain aluminium or zinc as the metal cation have also proved advantageous. However, complexes which contain iron as the metal cation are preferred because they display a particularly good corrosion protection action and because they are particularly cheap to manufacture.

40 Amongst the water-insoluble complex compounds of iron, aluminium or zinc those have proved particularly advantageous in which the ligand is an alkaline earth metal salt, preferably the barium salt, of 1 - nitroso - 2 - naphthol - 6 - sulphonic acid, having the formula:

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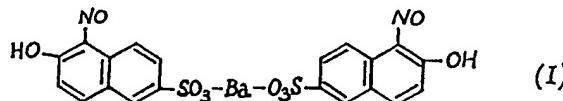
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In the case of these water-insoluble complex compounds of the alkaline earth metal salts of 1 - nitroso - 2 - naphthyl - 6 - sulphonic acid, those compounds in which the metal cation is iron have proved particularly valuable.

Any binder or coating material which is usually employed as a vehicle for corrosion inhibitors may be applied to the metal with the abovementioned corrosion inhibiting water-insoluble complex compounds.

The production of 1 - nitroso - 2 - naphthol and of its substitution products is known. Processes for the preparation of metal complexes of these compounds are also known. Such metal complexes have also already found use as pigments. Thus the use of nickel complexes of 1 - nitroso - 2 - naphthol is known from United Kingdom Patent Specification No. 1,047,114 and the use of iron complexes of 1 - nitroso - 2 - naphthol is known from United States Patent Specification No. 2,545,453. However, these complexes have not hitherto been employed as corrosion inhibitors.

Experiments carried out in connection with the invention have shown that a large number of soluble organic nitroso compounds are active as corrosion inhibitors. However, in lacquer technology, and for the purpose of coating agents, only their insoluble compounds are of interest, and these are at the same time also physiologically harmless as a result of their insolubility.

The corrosion inhibiting properties of organic nitroso compounds are presumably to be ascribed to the electrochemically active nitroso group. For this reason it was not to be expected that complex compounds of alpha - nitrosol - beta - naphthol and of the alkaline earth metal salts of 1 - nitroso - 2 - naphthol - 6 - sulphonic acid would be active as corrosion inhibitors because in the complexes the nitroso group is also involved in bonding the metal atom.

A further surprising fact is that the nitroso compounds used in the compositions and according to the process of the invention display a better protection against corrosion than the more expensive nitro compounds.

The necessary electrochemical interaction between the corrosion inhibitor of the invention and the metal, especially ferrous, surface to be protected is achieved by applying the inhibitor to the surface either without a carrier, or in conjunction with a carrier which should be liquid, at least initially, and may evaporate to leave a solid film in which the active inhibitor is embedded.

Thus, the inhibitor of the invention may be applied to an exposed metal surface, particularly a ferrous surface, by dusting, but it is preferred to disperse the compound in a liquid carrier, and to coat the surface to be protected with the dispersion. Water is the least expensive carrier and suitable where the inhibitor does not need protection against removal by mechanical stresses. Under suitable conditions, a small amount of water-soluble film-forming material, such as cellulose gum or other gums, may form an adequate film retaining the inhibitor after evaporation of the water, and a water-based latex of acrylic or other resins may be employed under less favourable conditions.

The complex compounds may also be incorporated in amounts of 0.5 to 3.0 percent (by weight) in organic coating compositions in which the vehicle is a volatile organic solvent, and the film forming substance may be selected from a wide variety of natural and/or synthetic resins capable of being dissolved or dispersed in the vehicle.

The Examples which follow are intended to compare two particularly advantageous corrosion inhibitors according to the invention with a corrosion inhibitor according to the prior art, as regards their respective protective action against corrosion.

The corrosion protection test carried out was based on the test method given in "Farbe und Lack", Volume 75 (1969). P. 945.

The pigment concentration was 37% by volume in the compositions of all three Examples and was adjusted by means of the oil absorption number as determined according to German Industrial Standard DIN 53,139. The compositions according to formulations 1 to 3 were applied to the bare surface of a bright steel sheet of deep drawing quality (Steel USt 1,405 m). Equal film thicknesses were in each case applied by means of the centrifugal lacquer coater. The samples were

dried in an oven at 120°C. for 30 minutes or in air for 7 days. Thereafter the corrosion protection test was carried out in the salt spray apparatus according to ASTM 117—64 (200 hours), or the condensation water exposure test according to DIN 50,018, using 0.2 litre of SO₂ (12 cycles).

5 The determination of the corrosion protection index, in per cent, which was carried out was based on DIN 53,210 (see "Farbe und Lack", 75, 1969, 945). 5

Corresponding corrosion protection indices were obtained on carrying out the test in air-drying binders (long-oil alkyd resins, i.e. polyesters of polyols and long-chain fatty acids in which the fatty acid content is more than 60%).

10 Example 1 10
A coating composition was prepared in a conventional manner from the following ingredients:

15 25.0 parts by weight of alkyd resin/melamine resin
29.0 parts by weight of solvent for the resins
2.0 parts by weight of iron chelate of 1-nitroso-2-naphthol 15
20.0 parts by weight of microtalc
24.0 parts by weight of barytes

Using this composition a corrosion protection index (CPI) of 73% was obtained.

20 Example 2 20
The procedures of Example 1 was followed with the following ingredients:

25 25.0 parts by weight of alkyd resin/melamine resin
29.0 parts by weight of solvent for the resins
2.0 parts by weight of zinc chelate of 1-nitroso-2-naphthol
20.0 parts by weight of microtalc
24.0 parts by weight of barytes 25

The corrosion protection index (CPI) was 68%.

Comparative Example 3

A coating composition for comparison purposes was prepared from the same ingredients as in Examples 1 and 2 except for the corrosion inhibitor. The composition contained:

30 35.0 parts by weight of alkyd resin/melamine resin
27.0 parts by weight of solvent for the resins
16.0 parts by weight of zinc potassium chromate
16.0 parts by weight of microtalc
16.0 parts by weight of barytes 35

The corrosion protection index (CPI) was 65%.

35 The CPI obtained using zinc potassium chromate, a known superior corrosion inhibitor was significantly lower than that obtained using the zinc chelate employed in Example 2 and much lower than that obtained with the iron chelate used in Example 1 under conditions which were closely comparable except for the much higher amount of inhibitor employed in Comparative Example 3. 40

An analogous relationship of CPI values of iron chelates with other chelates of the invention and with known inhibitors was found when the baking lacquer base of Examples 1 and 2 was replaced by an air drying varnish based on long-oil alkyd resin.

45 Results closely duplicating those of Examples 1 and 2 were achieved when the 1 - nitroso - 2 - naphthol chelates were replaced by chelates of the barium salt of 1 - nitroso - 2 - naphthol - 6 - sulphonic acid having the formula (I) herein. Useful, but less favourable results were achieved in corrosion tests of compounds in which barium was replaced by the other alkaline earth metals calcium and strontium. 50

WHAT WE CLAIM IS:—

1. A corrosion inhibitor composition comprising, as the corrosion-inhibiting compound, a water-insoluble complex compound of 1 - nitroso - 2 - naphthol, or of an alkaline earth metal salt of 1 - nitroso - 2 - naphthol - 6 - sulphonic acid with

- a metal cation, wherein the metal is iron, aluminium or zinc, in admixture with liquid carrier incorporating a film forming substance as hereinbefore described.
2. A composition according to Claim 1, in which the corrosion-inhibiting compound is an iron chelate of 1 - nitroso - 2 - naphthol.
- 5 3. A composition according to Claim 1, in which the corrosion-inhibiting compound is a water-insoluble complex compound of an alkaline earth metal salt of 1 - nitroso - 2 - naphthol - 6 - sulphonic acid with an iron cation.
- 10 4. A composition according to Claim 3, in which the alkaline earth metal salt is the barium salt of the formula (I) herein.
- 5 10 5. A corrosion inhibitor composition according to Claim 1 and substantially as hereinbefore described with reference to Examples 1 and 2.
- 15 15 6. A process for protecting a metal surface from corrosion which comprises applying to the surface a corrosion inhibitor comprising, as the corrosion-inhibiting compound, a water-insoluble complex compound of 1 - nitroso - 2 - naphthol or of an alkaline earth metal salt of 1 - nitroso - 2 - naphthol - 6 - sulphonic acid with a metal cation, wherein the metal is iron, aluminium or zinc.
- 20 7. A process according to Claim 6, in which the corrosion inhibitor includes a liquid carrier.
- 20 8. A process according to Claim 7, in which the carrier is water and the corrosion-inhibiting compound is dispersed therein.
- 25 9. A process according to Claim 8, in which a film-forming substance is dissolved in the water and the water is evaporated after application to the metal surface.
10. A process according to Claim 7, in which the carrier is a volatile organic solvent having a film-forming material dispersed therein.
- 25 11. A process according to Claim 10, in which the film-forming material is an alkyd resin/melamine resin mixture.
12. A process according to claim 6, in which the corrosion inhibitor is applied to an exposed metal surface by dusting.
- 30 13. A process according to any one of Claims 6 to 12, in which the metal cation is iron.
- 30 14. A process for protecting a metal surface from corrosion according to Claim 6 and substantially as hereinbefore described with reference to Examples 1 and 2.
- 35 15. Metal articles whose surfaces are coated with a corrosion inhibitor composition according to any one of Claims 1 to 5 or by a process according to any one of Claims 6 to 14.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

DERWENT-ACC-NO: 1976-30327X

DERWENT-WEEK: 200300

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TITLE: Phosphate corrosion preventives for iron and steel -
using barium zinc phosphate contg. cobalt or magnesium
phosphate (BE050476)]

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PRIORITY-DATA: 1974DE-2447208 (October 3, 1974)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES
MAIN-IPC			
DE 2447208 A	April 15, 1976	N/A	000 N/A
BE 834177 A	April 5, 1976	N/A	000 N/A
FR 2286867 A	June 4, 1976	N/A	000 N/A

INT-CL (IPC): C01B025/26, C09D005/08 , C23F007/08 , C23F015/00

ABSTRACTED-PUB-NO: DE 2447208A

BASIC-ABSTRACT:

Corrosion-preventive agent contg. phosphates, the novelty being that it contains phosphates of formula BaZn_{2-n}Mn II(PO₄)₂, where MII is at least one of the divalent metals Co and Mg, and n is 0-0.8. pref. 0.1-0.6. Pref. materials are (a) BaZn₂₋₍Con(PO₄)₂; (b) BaZn_{2-n}Mgn(PO₄)₂; (c) BaZn₂PO₄. The agent may also contain a binder with wt. ratio binder: pigment plus filler min. 0.1, esp. 0.4-3, the pref. binder being polyvinylacetal or polyvinylbutyral; the agent may also contain phosphoric acid, and its pref. application is on metals. Agents are shop-primers or wash-primers, i.e. self-etching primers, esp. for iron and steel.

Improved corrosion resistance as compared with existing phosphates, effective over long periods and materials which may cause cancer need not be used.

DERWENT-CLASS: A97 E32 M14

CPI-CODES: A12-B04A; E31-K05; M13-H05; M14-D02; M14-F02;